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(54) **GAS OIL ADDITIVE AND GAS OIL COMPOSITION**

(57) Pertaining to a gas oil additive for gas oil having a sulfur content of 0.2% by weight or less, characterized in that the gas oil additive contains a compound containing a hydrocarbon group having 10 to 22 carbon atoms, amide group, and hydroxyl group on a carbon atom in β-position to nitrogen atom of the amide group; a gas oil composition containing the gas oil additive; and a method of reducing wear in a fuel injection pump or deterging a fuel injection nozzle, each comprising using the gas oil composition. By using the gas oil composition of the present invention, there can be exhibited effects in reducing wear of fuel pumps in a system using a gas oil likely to cause wear in fuel pumps, the gas oil having a sulfur content of 0.2% by weight or less, particularly 0.05% by weight or less, and detergency effects of an injection nozzle of diesel engines.

Description

TECHNICAL FIELD

[0001] The present invention relates to a gas oil additive and a gas oil composition which can be effective in reducing wear of metal surfaces contacting the composition in a system using a low-sulfur gas oil, and effective in deterging a fuel injection nozzle.

BACKGROUND ART

[0002] In recent years, there has arisen a problem in environmental pollution by nitrogen oxides (NO_x), sulfur oxides (SO_x) and particulate matters each contained in an exhaust gas coming from diesel cars. Concretely, there pose problems in corrosion and wear of metals, and acid rain owing to acid substances formed by the combustion of sulfur components contained in the gas oil used as a fuel for engines. Up to now, nitrogen oxides and sulfur oxides contained in exhaust gas have been regulated, and a new regulation with respect to a particulate matter has been added. As to a countermeasure for this regulation with respect to the particulate matter, there has been firstly proposed to decrease the amount of the sulfur oxides in exhaust gas, in other word, to cut down the sulfur content in a gas oil in stages. Further, along with the amendment (1990) of "the Clean Air Act" in the U.S.A., an amendment that the sulfur content of a gas oil must be 0.05% by weight or less as a quality standard for the gas oil was made. In the above circumstances, it is anticipated that there will be taken a countermeasure in stages in Japan regarding the quality of the gas oil to restrict the sulfur content firstly to 0.2% by weight or less, and further to 0.2% by weight or less within this century. In fact, gas oils having low sulfur contents have been made commercially available in, e.g., Europe and the U.S.A. However, when the sulfur content in the gas oil is decreased, there arises a new problem of fuel injection pump seizures owing to deficiency of the lubricity of the gas oil as described in SAE PAPER 942016. In Sweden, in fact, several thousands of cars have encountered troubles caused by the deficiency of the lubricity of the low-sulfur, low-aromatic compounds-containing gas oil as an environmental-protecting fuel. Meanwhile, in Japan, low-sulfur gas oils for diesel engines presently have not become popular. When the low-sulfur gas oils for diesel engines are used in the near future, it is anticipated that there arise problems of fuel pump seizures or wear of metal surfaces contacting the composition.

[0003] In addition, stains of the fuel injection nozzle for the diesel engines, mainly cokes, cause significant mal-affects to its performance. When the cokes are formed, the contents of black smoke in the exhaust gas, sulfates derived from sulfur in the fuel, and hydrocarbons formed by partial combustion of fuels and lubricating oils (those hydrocarbons are collectively referred to "particulate matters") are increased.

[0004] In order to solve the above problems, there has been proposed an oxyalkylene compound of an alkylamine in Japanese Patent Examined Publication No. 3-49317 as an additive for imparting a detergency effect of a fuel injection nozzle for diesel engines. However, the detergency effect cannot be said to be satisfactory.

[0005] Japanese Patent Examined Publication No. 63-32837 discloses a nitrogen-containing polyoxyethylene compound as a gas oil additive for decreasing particulate matters in the exhaust gas for diesel engines. However, this publication is completely silent on the low-sulfur gas oil having a sulfur content of 0.2% by weight or less in the gas oil. It rather mentions the application to a gas oil according to JIS K 2204 (level required at the time of 1988). There has been reported that the JIS standard of the sulfur content in the gas oil of those days is 0. 5% by weight or less, and the average sulfur content of the commercially available gas oil of those days is 0.4% by weight on average (see *Nisseki Review*, **30**, 6).

[0006] From the above, it is found that the problems of wear accompanied with low sulfurization of the gas oil are not considered at all.

[0007] As a prior art concerning the reduction in wear, W0941760 discloses the use of an ester obtained from a carboxylic acid having 2 to 50 carbon atoms and an alcohol as an agent for reducing wear in low-sulfur diesel gas oils. However, its performance in wear resistance cannot be said to be satisfactory. As to fuel additives, there has been disclosed a composition comprising cyclopentyl ester of formic acid, a condensate obtained from triethanolamine and oleic acid, and a spindle oil as an additive for diesel fuels for the purpose of improving exhaust gas (Japanese Patent Laid-Open No. 50-161504). However, this publication is completely silent with regard to wear caused by the low-sulfur gas oil. Moreover, since the sulfur content in the gas oil subjected to use is high, the necessity for countermeasure for preventing wear caused by the decreased sulfur content is presumably not particularly considered.

[0008] Further, Japanese Patent Laid-Open Nos. 55-082191 and 55-00780 and W09307238 each discloses the use of an alkanolamide as an emulsifier for emulsion fuels. U.S. Patent No. 4204481 discloses the use of an oleic acid amide of diethanolamine as a wear inhibitor for alcohol fuels. However, these publications are silent with regard to the use in the low-sulfur gas oil.

[0009] In addition, it has been found that when the low-sulfur gas oil without including additives is kept standing under exposure, the insoluble components are precipitated in the gas oil and form a sludge, so that an improvement in the

storage stability of the gas oil is considered to be required.

DISCLOSURE OF THE INVENTION

[0010] Accordingly, an object of the present invention is to provide a gas oil additive and a gas oil composition which are effective in reducing a wear amount of metal surfaces contacting the composition in a system using a low-sulfur gas oil; effective in deterging a fuel injection nozzle for the diesel engines; and effective in the improvement in the storage stability of the low-sulfur gas oil. There are no prior arts with regard to the object of the present invention.

[0011] As a result of intensive studies in order to solve the above problems, the present inventors have found that the gas oil composition for diesel engines having an excellent effect of reducing wear amounts, an excellent detergency effect of a fuel injection nozzle, and an excellent effect for storage stability can be obtained by including a particular compound as a gas oil additive in a gas oil having a sulfur content of 0.2% by weight or less. The present invention has been completed based on these findings.

[0012] Specifically, the gist of the present invention pertains to the following:

(1) A gas oil additive for gas oil having a sulfur content of 0.2% by weight or less, characterized in that the gas oil additive contains a compound containing a hydrocarbon group having 10 to 22 carbon atoms, amide group, and hydroxyl group on a carbon atom in β-position to nitrogen atom of the amide group;

(2) The gas oil additive described in item (1) above, characterized in that the compound as recited in item (1) above is a condensate obtained from one or more monovalent fatty acids having 10 to 22 carbon atoms and one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine;

(3) The gas oil additive described in item (2) above, characterized in that the monovalent fatty acid as recited in item (2) above is a mixture of fatty acids comprising 70 to 90% by weight of a fatty acid having one unsaturated bond; 5 to 10% by weight of a fatty acid having two unsaturated bonds; and 5 to 20% by weight of a saturated fatty acid;

(4) The gas oil additive described in item (3) above, characterized in that the mixture of fatty acids contains 68 to 78% by weight of 9-octadecenoic acid;

(5) The gas oil additive described in item (1) above, characterized in that the compound as recited in item (1) above is a condensate obtained from a fatty acid ester corresponding to the fatty acid as recited in item (2) or item (3) above and one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine;

(6) The gas oil additive described in item (5) above, characterized in that the fatty acid ester contains 68 to 78% by weight of 9-octadecenoic acid ester;

(7) The gas oil additive described in any one of items (2) to (6) above, characterized in that a total content of one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine which remain therein is 5% by weight or less;

(8) The gas oil additive described in item (1) above, characterized in that the gas oil additive further contains, in addition to the compound as recited in item (1) above, Compound (B) defined below:

one or more compounds selected from the group consisting of nonionic surfactants having an HLB of 3 to 13; aliphatic amines having 8 to 28 carbon atoms; and alkylene oxide adducts of an aliphatic amine having 8 to 28 carbon atoms, an alkylene oxide moiety having 2 to 3 carbon atoms and a molar addition of 50 mol or less, and that a weight ratio of (A)/(B) is from 1/0.01 to 1/0.5, the compound as recited in item (1) above being defined as Compound (A);

(9) The gas oil additive described in item (8) above, wherein Compound (A) is a condensate as defined in any one of items (2) to (7) above;

(10) The gas oil additive described in any one of items (1) to (9) above, wherein a sulfur content of the gas oil is 0.05% by weight or less;

(11) The gas oil additive described in any one of items (1) to (10) above, wherein the gas oil additive is used for the purposes of reducing wear on the contacting surfaces of a metal and deterging a fuel injection nozzle;

(12) A gas oil composition having a function of reducing wear and a function of deterging stains, characterized in that the gas oil composition comprises a gas oil having a sulfur content of 0.2% by weight or less and the gas oil additive described in any one of items (1) to (11) above, wherein a content of the gas oil additive is from 0.001 to 1.0 part by weight, based on 100 parts by weight of the gas oil;

(13) The gas oil composition described in item (12) above, characterized in that a content of the gas oil additive is from 0.001 to 0.1 parts by weight, based on 100 parts by weight of the gas oil;

(14) The gas oil composition described in item (12) or (13) above, wherein the gas oil has a sulfur content of 0.05% by weight or less;

(15) A method of reducing wear in a fuel injection pump comprising using the gas oil composition described in any one of items (12) to (14) above; and

(16) A method of deterging a fuel injection nozzle comprising using the gas oil composition described in any one of items (12) to (14) above.

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] The present invention will be described in detail below.

[0014] The gas oil additive of the present invention comprises Compound A described below, or it may further comprise Compound B in addition to Compound A. Compound A is a compound containing a hydrocarbon group having 10 to 22 carbon atoms, amide group, and hydroxyl group on a carbon atom in β-position to nitrogen atom of the amide group in a molecule. Examples of the compounds include condensates obtained from one or more fatty acids and one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine.

[0015] Here, the term "fatty acid" refers to a linear or branched, monovalent fatty acid having 10 to 22 carbon atoms, which may be a saturated fatty acid or an unsaturated fatty acid, respectively. Concrete examples of the fatty acids include monovalent fatty acids containing a linear or branched, saturated alkyl group having 10 to 22 carbon atoms, including decanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, arachic acid, behenic acid, or the like; and unsaturated fatty acids having 10 to 22 carbon atoms, including oleic acid, erucic acid, linoelaidic acid, linoleic acid, or the like. Also, in the present invention, fatty acid esters corresponding to the fatty acids mentioned above may be used instead of, or together with, these fatty acids. Examples of the fatty acid esters include esters obtained from the fatty acids mentioned above and alcohols having 1 to 3 carbon atoms.

[0016] In order to exhibit an effect for preventing wear in the present invention, it is necessary that an additive is dissolved in the gas oil, and that the additive has the effect for preventing wear.

[0017] In the case of using the fatty acid alone,

(1) from the viewpoint of the effect for preventing wear, a linear, saturated fatty acid having 12 to 22 carbon atoms or a linear, unsaturated fatty acid having 16 to 20 carbon atoms is preferably used; and in particular, the linear, saturated fatty acid having 12 to 22 carbon atoms is more preferably used, and

(2) from the viewpoint of the solubility to the gas oil, a linear, saturated fatty acid having 10 to 14 carbon atoms, or a linear, unsaturated fatty acid having 10 to 22 carbon atoms is preferably used, and in particular, the linear, unsaturated fatty acid having 10 to 22 carbon atoms is more preferably used.

[0018] Moreover, from the viewpoints of both an effect for preventing wear and solubility, it is preferable to use a linear, saturated fatty acid having 12 to 14 carbon atoms, more preferably lauric acid having 12 carbon atoms; or a linear, unsaturated fatty acid having 16 to 20 carbon atoms, more preferably 9-octadecenoic acid having 18 carbon atoms.

[0019] Further, an embodiment wherein two or more fatty acids are used may be included in the present invention. In this case, from the viewpoints of solubility to the gas oil, an effect for preventing wear on the contacting surfaces of a metal, and a detergency effect of a fuel injection nozzle, it is preferable to use a mixture of fatty acids wherein to a total amount of the fatty acids, the weight proportion of a fatty acid having one unsaturated bond is 70 to 90% by weight; the weight proportion of a fatty acid having two unsaturated bonds is 5 to 10% by weight; and the weight proportion of a saturated fatty acid is 5 to 20% by weight. Moreover, as to the number of carbon atoms for these fatty acids, it is more preferred that the number of carbon atoms of the fatty acid having one unsaturated bond is 14, 16 or 18; the number of carbon atoms of the fatty acid having two unsaturated bonds is 18; and the number of carbon atoms of the saturated fatty acid is 14, 16 or 18. From the viewpoint of preventing wear even more effectively, the saturated fatty acid is preferably used, and from the viewpoint of high solubility to the gas oil, the unsaturated fatty acid is preferably used. Therefore, the gas oil additives having excellent performance satisfying all of the solubility to gas oil, the wear resistance effect and the detergency effect can be obtained by using the mixture of the fatty acids mentioned above of the saturated fatty acid and the unsaturated fatty acid. Among them, the additives containing 68 to 78% by weight of 9-octadecenoic acid to a total amount of the fatty acids, including fatty acid esters described below, are particularly preferably used. Also, when the fatty acid ester is used as described below, the additives containing 68 to 78% by weight of 9-octadecenoic acid ester to the total amount of the fatty acids or the fatty acid esters are preferably used.

[0020] The amine compounds which are used for condensation include one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine.

[0021] Concrete examples of the condensates obtained from fatty acids and one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine include the following: When the condensates are obtained from a fatty acid and monoethanolamine, examples thereof include fatty acid amides of monoethanolamine, fatty acid esters of monoethanolamine, fatty acid amide-esters of monoethanolamine, and the like.

In the present invention, the fatty acid amides of monoethanolamine are used as a component. Also, when the condensates are obtained from a fatty acid and diethanolamine, examples thereof include fatty acid amides of diethanolamine, fatty acid esters of diethanolamine, fatty acid amide-esters of diethanolamine, and the like. In the present invention, the fatty acid amides of diethanolamine are used as a component. The condensate obtained from a fatty acid and monoethanolamine and diethanolamine is a mixture of the condensates mentioned above. Also, when the condensates are obtained from a fatty acid and mono-2-propanolamine, examples thereof include fatty acid amides of mono-2-propanolamine, fatty acid esters of mono-2-propanolamine, fatty acid amide-esters of mono-2-propanolamine, and the like. In the present invention, the fatty acid amides of mono-2-propanolamine are used as a component. Also, when the condensates are obtained from a fatty acid and di-2-propanolamine, examples thereof include fatty acid amides of di-2-propanolamine, fatty acid esters of di-2-propanolamine, fatty acid amide-esters of di-2-propanolamine, and the like. In the present invention, the fatty acid amides of di-2-propanolamine are used as a component.

[0022] Compound A used in the gas oil additives of the present invention can be prepared, for example, by following method.

[0023] In other words, a desired condensate can be obtained by a process comprising heating a fatty acid together with one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine, and carrying out amidation reaction while removing water formed. Also, for example, a desired condensate can be obtained in a higher yield by a process comprising reacting a fatty acid ester such as a methyl ester of a fatty acid together with one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine with heating while removing methanol.

[0024] When the total content of one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine which are unreacted and remain in the reaction product exceeds 5% by weight, the effect for reducing wear and the detergency effect of a fuel injection nozzle are drastically declined. Therefore, it is desired that the total remaining amount of one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine is controlled to 5% by weight or less, preferably 3% by weight or less, more preferably 1% by weight or less, most preferably 0.5% by weight or less.

[0025] In order to reduce the remaining amount of one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine in the desired condensates as much as possible, and to obtain fatty acid amides, the desired condensates, in high yields, methods for reacting a fatty acid ester with one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine are preferably employed. It is preferred that examples of the fatty acid esters are esters obtained from a fatty acid and a lower alcohol, such as methanol, ethanol and propanol.

[0026] Compounds B are one or more compounds selected from the group consisting of nonionic surfactants having an HLB of 3 to 13; aliphatic amines having 8 to 28 carbon atoms; and alkylene oxide adducts of an aliphatic amine having 8 to 28 carbon atoms, of which the alkylene oxide moiety has 2 to 3 carbon atoms with molar addition of 50 mol or less. Here, concrete examples of the nonionic surfactants having an HLB of 3 to 13 include polyoxyalkylene alkyl ethers, polyoxyalkylene alkenyl ethers, polyoxyalkylene alkylphenyl ethers, sorbitan fatty acid esters, polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbitol fatty acid esters, polyoxyalkylene fatty acid esters, glycerol fatty acid esters, and the like.

[0027] More concretely, it is desired that the polyoxyalkylene alkyl ethers and the polyoxyalkylene alkenyl ethers are alkylene oxide adducts of which the alkylene oxide moiety has 2 to 3 carbon atoms, the adducts having a linear or branched, alkyl group or alkenyl group having 8 to 30 carbon atoms, more preferably 10 to 22 carbon atoms, and still more preferably alkylene oxide adducts having a linear alkyl group or alkenyl group having 10 to 22 carbon atoms. Still more concrete examples of the polyoxyalkylene alkyl ethers and the polyoxyalkylene alkenyl ethers include polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, and the like, and each of those listed above may have an oxypropylene group in a molecule. The HLB is preferably 5 to 13, more preferably 7 to 12.

[0028] The polyoxyalkylene alkylphenyl ethers are alkylene oxide adducts of which alkylene oxide moiety has 2 to 3 carbon atoms, the adducts having an alkylphenyl group having 8 to 30 carbon atoms. More concrete examples thereof include polyoxyalkylene octylphenyl ether, polyoxyalkylene nonylphenyl ether, and the like. The HLB is preferably 5 to 13, more preferably 7 to 12.

[0029] The sorbitan fatty acid esters and the polyoxyalkylene sorbitan fatty acid esters are sorbitan fatty acid esters and fatty acid esters of sorbitan alkylene oxide adducts of which the alkylene oxide moiety has 2 to 3 atoms, each of the fatty acid esters having 10 to 28 carbon atoms. It is desired that the fatty acid ester has 10 to 22 carbon atoms, and it is more desired that a linear, saturated fatty acid ester has 12 to 18 carbon atoms, or a linear, unsaturated fatty acid ester has 14 to 20 carbon atoms.

[0030] Similarly, the polyoxyalkylene sorbitol fatty acid esters are fatty acid esters of sorbitol alkylene oxide adducts of which the alkylene oxide moiety has 2 to 3 carbon atoms, each of the fatty acid esters having 10 to 28 carbon atoms. It is desired that a linear, saturated or unsaturated fatty acid ester has 10 to 20 carbon atoms, and it is more desired that

a linear, saturated fatty acid ester has 12 to 18 carbon atoms, or a linear, unsaturated fatty acid ester has 14 to 20 carbon atoms.

[0031] The polyoxyalkylene fatty acid esters are alkylene oxide adducts of which alkylene oxide moiety has 2 to 3 carbon atoms, and the fatty acid moiety has 10 to 28 carbon atoms. It is desired that a linear, saturated or unsaturated fatty acid ester has 12 to 20 carbon atoms, and it is more desired that a linear, saturated fatty acid ester has 12 to 18 carbon atoms or a linear, unsaturated fatty acid ester has 14 to 20 carbon atoms.

[0032] The glycerol fatty acid esters are mono-, di-, triesters obtained from glycerol and fatty acids having 10 to 28 carbon atoms, preferably esters obtained from a linear, saturated or unsaturated fatty acid having 12 to 20 carbon atoms and glycerol, more preferably mono- and diesters thereof. Preferred examples of the fatty acids used in esterification with glycerol include lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, and the like. A linear, unsaturated fatty acid having 14 to 20 carbon atoms is more preferably used.

[0033] Also, the aliphatic amines having 8 to 28 carbon atoms are aliphatic amines having an aliphatic, saturated hydrocarbon group or aliphatic, unsaturated hydrocarbon group having 8 to 28 carbon atoms. Concrete examples of the aliphatic amines include decylamine, laurylamine, myristylamine, cetylamine, stearylamine, oleylamine, beef tallow amine, hydrogenated beef tallow amine, and the like. A saturated or unsaturated, aliphatic amine having 12 to 20 carbon atoms is preferably used, and an unsaturated, aliphatic amine having 14 to 20 carbon atoms is more preferably used.

[0034] In addition, there are included the alkylene oxide adducts of the aliphatic amines mentioned above, of which the alkylene oxide moiety has 2 to 3 carbon atoms with molar addition of 50 mol or less, preferably the alkylene oxide adducts with molar addition of 20 mol or less, more preferably the alkylene oxide adducts with molar addition of 10 mol or less.

[0035] Incidentally, it is desired that concrete examples of alkylene oxide adducts in Compound B used in the present invention include ethylene oxide adducts and propylene oxide adducts. The alkylene oxide may be used alone or in combination. When using ethylene oxide in combination with propylene oxide, the monomeric units may be polymerized by block addition or random addition.

[0036] Even when using Compound A alone, the effect for reducing the wear amount and the detergency effect of a fuel injection nozzle are well exhibited. However, in order to further improve the effect for reducing wear and the storage stability of the low-sulfur gas oil, Compound A is preferably used in combination with Compound B. The blending amount of Compound B is suitably determined according to the properties of the gas oil used, and the weight ratio of Compound A/Compound B is preferably from 1/0.01 to 1/0.5, more preferably from 1/0.02 to 1/0.3, particularly preferably from 1/0.03 to 1/0.2.

[0037] The amount of the gas oil additive of the present invention is not particularly limited, and the gas oil additive can be used in an amount sufficient to suppress at least the wear of the contacting surfaces of a metal by the gas oil. Concretely, it is desired to use the gas oil additive in an amount of from 0.001 to 0.1 parts by weight, preferably from 0.001 to 0.05 parts by weight, based on 100 parts by weight of the gas oil. When the amount is less than 0.001 parts by weight, the effect for reducing wear is lessened. On the other hand, when the amount exceeds 0.1 parts by weight, the effect for reducing wear is not increased, thereby making it economically disadvantageous.

[0038] As to the detergency of a fuel injection nozzle, for the purposes of using a new nozzle and maintaining the detergency of the nozzle, it is desired to use the gas oil additive in an amount of from 0.001 to 0.1 parts by weight, preferably from 0.005 to 0.05 parts by weight, based on 100 parts by weight of the gas oil, from the viewpoints of the above effects and economic advantages. When stains are formed on the nozzle, in order to remove the stains, it is desired to use the gas oil additive in an amount of from 0.001 to 1.0 part by weight, desirably from 0.05 to 1.0 part by weight, based on 100 parts by weight of the gas oil.

[0039] The term gas oil used in the present invention refers to a low-sulfur gas oil having a sulfur content of 0.2% by weight or less, particularly 0.05% by weight or less, is desirably used. Examples of the low-sulfur gas oil which can be used in the present invention include those prepared by a method comprising, using a hydrodesulfurization apparatus, subjecting a gas oil distillate resulting from distillation of a crude oil under atmospheric pressure to, for instance, (1) hydrodesulfurization at a high reaction temperature; (2) hydrodesulfurization under a high hydrogen partial pressure; (3) hydrodesulfurization using a hydrodesulfurization catalyst having high activity, or the like. As long as the measured value of the sulfur content as determined by a radiation-type excitation method in accordance with JIS K 2541 is 0.2% by weight or less, particularly 0.05% by weight or less, the methods for desulfurization are not particularly limited.

[0040] In the gas oil additives or the gas oil composition of the present invention, various additives can be suitably used. Examples of such additives include antioxidants, conductivity improvers, metal deactivators, freezing-controlling additives, cetane number improvers, combustion improvers (including smoke controllers), surfactants/dispersants, manifold system detergents, corrosion inhibitors, demulsifiers, top cylinder lubricants, and dyes.

[0041] Among the antioxidants, phenolic antioxidants are suitably used, and other gas oil-soluble antioxidants other than phenolic antioxidants can also be used. Examples of the suitable antioxidants other than phenolic antioxidants include amine antioxidants and other similar substances. The amount of the antioxidant is preferably in range of from

about 2.8 g to about 28 g per 1000 liters of the gas oil composition. However, the antioxidant can be used exceeding the upper limit of this range as occasion demands.

[0042] The conductivity improver is an additive to be dissolved in the gas oil composition in order to elevate the conductivity of the resulting gas oil composition to an appropriate range, for example, from about 50 ps/m to about 600 ps/m, as measured according to ASTEM D-2624. The amount thereof is preferably in a range of from about 5 g to about 50 g per 1000 liters of the gas oil composition.

[0043] The function mechanism of the compound of the present invention is considered to be as follows. The compound of the present invention adsorbs to the metal surfaces via OH group in the compound in the present invention, and the adsorbed compound forms a lubricative film, which presumably provides the effect for reducing wear. Therefore, the compound having OH group in a molecule is effective in adsorbing to the metal. Particularly, the compound having a structure such that the OH group is located on the carbon atom at a β-position to the nitrogen atom, and having an ability of forming a chelate to the metal is effective in adsorbing to the metal surfaces. Further, the compounds having two OH groups are preferably used. Further, in this structure, the OH group and the nitrogen atom collaborate to bind with the stains to form a chelate compound, whereby the stains are made soluble and dispersible, so that the detergency effect of a fuel injection nozzle of diesel engines is presumably exhibited. Also, in the effects mentioned above, the hydrocarbon group of the fatty acid plays a large role in dissolving and dispersing the compound of the present invention in the gas oil.

[0044] Further, when considering the storage stability of the gas oil, turbidity in the low-sulfur gas oil under exposure is formed by the fact that the components in the gas oil are subject to deterioration by light and oxygen to form polar substances and grow, which subsequently are precipitated in the gas oil as an insoluble component in the gas oil. Compound B mentioned above stabilizes this polar substance in dispersion and prevents the insoluble components from depositing.

[0045] When the gas oil additive of the present invention is used in the gas oil wherein the sulfur content in the gas oil is 0.2% by weight or less, particularly 0.05% by weight or less, the remarkable effect for reducing wear in a fuel injection pump and the remarkable detergency effect of a fuel injection nozzle can be obtained. Also, the gas oil with improved storage stability can be obtained.

[0046] The present invention will be further described in detail by means of preparation examples, examples, comparative examples, and test examples, without intending to restrict the scope of the present invention to these working examples, and the like.

Examples Using Compound A Alone

Preparation Example 1

[0047] A two-liter four-necked flask was charged with 2.5 mol of 9-octadecenoic acid and 2.5 mol of diethanolamine, and the temperature of the contents was raised while stirring the resulting mixture in a nitrogen gas atmosphere. Subsequently, the components were reacted while dehydrating under a reduced pressure of 30 mmHg at 150°C. Having confirmed that no more water is distilled off, the reaction was terminated, to give a reaction product. The resulting reaction product was analyzed by GPC analysis (gel permeation chromatogram), to give 40% of N,N-bis-(2-hydroxyethyl)oleamide. As to the other components, an amide-ester compound was obtained as a by-product. The amount of diethanolamine remaining in the resulting mixture was 0.7% by weight. The amount of diethanolamine remaining in the resulting mixture was assayed by GPC analysis (the same method being employed for the following Preparation Examples).

Preparation Example 2

[0048] The same procedures as in Preparation Example 1 were carried out except that 2.5 mol of a mixed acid (9-octadecenoic acid/1-eicosenoic acid/13-docosenoic acid = 40/15/45) and 2.5 mol of diethanolamine were reacted to give reaction products. 43% Of N,N-bis-(2-hydroxyethyl)-fatty acid amides were obtained as determined by GPC analysis. As to the other components, amide-ester compounds were obtained as by-products. The amount of diethanolamine remaining in the resulting mixture was 0.6% by weight.

Preparation Example 3

[0049] A two-liter four-necked flask was charged with 2.5 mol of methyl 9-octadecenoate, 2.5 mol of diethanolamine and 0.03 mol of sodium methoxide as a catalyst, and the temperature of the contents was raised while stirring the resulting mixture in a nitrogen gas atmosphere. Subsequently, the components were reacted while removing methanol under a reduced pressure of 30 mmHg at 110°C. Having confirmed that no more methanol is distilled off, the reaction

was terminated, and the catalyst was adsorbed by an alkali adsorbent and removed from the reaction mixture, to give a reaction product. The resulting reaction product was analyzed by GPC analysis (gel permeation chromatogram), to give 85% of N,N-bis-(2-hydroxyethyl)oleamide. As to the other components, an amide-ester compound was obtained as a by-product. The amount of diethanolamine remaining in the resulting mixture was 0.2% by weight.

Preparation Example 4

[0050] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of a mixed acid (methyl 9-octadecenoate/methyl 11-eicosenoate/methyl 13-docosenoate = 40/15/45) and 2.5 mol of diethanolamine were reacted to give reaction products. 83% Of N,N-bis-(2-hydroxyethyl)-fatty acid amides were obtained as determined by GPC analysis. As to the other components, amide-ester compounds were obtained as by-products. The amount of diethanolamine remaining in the resulting mixture was 0.3% by weight.

Preparation Example 5

[0051] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of a mixed acid (methyl tetradecanoate/methyl hexadecanoate/methyl octadecanoate/methyl 5-tetradecenoate/7-hexadecenoic acid/methyl 9-octadecenoate/9, 12-octadecadienoic acid = 3/6/1/3/7/72/8) and 2.5 mol of diethanolamine were reacted to give reaction products. 84% Of N,N-bis-(2-hydroxyethyl)-fatty acid amides were obtained as determined by GPC analysis. As to the other components, amide-ester compounds were obtained as by-products. The amount of diethanolamine remaining in the resulting mixture was 0.2% by weight.

Preparation Example 6

[0052] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of methyl laurate and 2.5 mol of diethanolamine were reacted to give a reaction product. 80% Of N,N-bis-(2-hydroxyethyl)-fatty acid amide was obtained as determined by GPC analysis. As to the other components, an amide-ester compound was obtained as a by-product. The amount of diethanolamine remaining in the resulting mixture was 0.4% by weight.

Preparation Example 7

[0053] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of methyl stearate and 2.5 mol of diethanolamine were reacted to give a reaction product. 81% Of N,N-bis-(2-hydroxyethyl)-fatty acid amide was obtained as determined by GPC analysis. As to the other components, an amide-ester compound was obtained as a by-product. The amount of diethanolamine remaining in the resulting mixture was 0.3% by weight.

Preparation Example 8

[0054] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of methyl isostearate and 2.5 mol of diethanolamine were reacted to give a reaction product. 79% Of N,N-bis-(2-hydroxyethyl)-fatty acid amide was obtained as determined by GPC analysis. As to the other components, an amide-ester compound was obtained as a by-product. The amount of diethanolamine remaining in the resulting mixture was 0.3% by weight.

Preparation Example 9

[0055] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of a mixed acid (methyl tetradecanoate/methyl hexadecanoate/methyl octadecanoate/methyl 5-tetradecenoate/7-hexadecenoic acid/methyl 9-octadecenoate/9,12-octadecadienoic acid = 3/6/1/3/7/72/8) and 2.5 mol of monoethanolamine were reacted to give reaction products. 84% Of N,N-bis-(2-hydroxyethyl)-fatty acid amides were obtained as determined by GPC analysis. As to the other components, amide-ester compounds were obtained as by-products. The amount of monoethanolamine remaining in the resulting mixture was 0.4% by weight.

Preparation Example 10

[0056] The same procedures as in Preparation Example 3 were carried out except that 2.5 mol of a mixed acid (methyl tetradecanoate/methyl hexadecanoate/methyl octadecanoate/methyl 5-tetradecenoate/7-hexadecenoic acid/methyl 9-octadecenoate/9, 12-octadecadienoic acid = 3/6/1/3/7/72/8) and 2.5 mol of di-2-propanolamine were reacted to give reaction products. 81% Of N,N-bis-(2-hydroxyethyl)-fatty acid amides were obtained as determined by GPC analysis.

As to the other components, amide-ester compounds were obtained as by-products. The amount of di-2-propanolamine remaining in the resulting mixture was 0.3% by weight.

Preparation Example 11

[0057] The similar procedures as in Example 5 were carried out except that methanol was not sufficiently removed, to prepare a reaction product in which diethanolamine remained in the reaction product in an amount of 1.5% by weight or more.

Comparative Product 1

[0058] A commercially available oleic acid monoglyceride ("SUNSOFT No. 8070" manufactured by Taiyo Kagaku Co., Ltd.) was used.
[0059] Monoglyceride content: 90% by weight or more (according to catalogue).

Comparative Product 2

[0060] A commercially available oleic acid amide (manufactured by Kao Corporation) was used.

Evaluation of Single Compound A

[Evaluation I of Wear Reduction Effects]

Examples 1 to 14 and Comparative Examples 1 to 4

[0061] Each of Compounds 1 to 10 usable in the present invention was added in an amount shown in Table 1, to 100 parts by weight of a low-sulfur gas oil having a sulfur content of 0.04% by weight or 0.20% by weight, to prepare a composition. The resulting composition was subjected to a standard test known as a ball-lubricity evaluation test using a cylinder. The test procedures are in accordance with ASTM D 5001-90. In this test, the scar diameter was measured. Here, the smaller the scar diameter, the more effective the additives become regarding wear prevention. In order to make sure that each of these gas oil compositions has excellent storage stability, the gas oil composition was stored at 25°C for one month under a surrounding light condition prior to carrying out the lubricity test. It was confirmed that the formation of precipitates, deterioration by oxidation, discoloration, and the like were not observed in each of the compositions (with the exception for Preparation Example 7 where a slight turbidity was found, so that the composition was heated again to 40°C and then tested). The results obtained are shown in Table 1. The results indicate that each of the gas oil compositions containing Compounds of the present invention having a sulfur content of 0.04% by weight or 0.20% by weight has good wear resistance. The scar diameter of each of the gas oil compositions of Examples 1 to 10 of the present invention was from 0.29 mm to 0.52 mm, so that excellent wear resistance can be observed in these compositions. Here, in cases of Examples 1 and 2 using Compounds of Preparation Examples 1 and 2 derived from fatty acids, the performance in preventing wear was slightly reduced as compared with Compounds of Preparation Examples 3 and 4 derived from methyl ester of fatty acids. In the case of Example 11 where Preparation Example 11 in which diethanolamine remained in an amount of 1% by weight or more was used, although some effects can be observed as compared with Comparative Example 1 where no additives were included, the performance in preventing wear was somewhat weak as compared with other Examples. As Comparative Examples, similar tests were carried out with a low-sulfur gas oil (sulfur content: 0.04% by weight) used as a base, without including any of inventive products, and with a presently generally commercially available gas oil having a sulfur content of 0.2% by weight. As a result, the scar diameters were 0.82 mm and 0.65 mm, respectively. Also, the scar diameter using Comparative Product 1 was 0.61 mm, so that it was found that these comparative gas oil compositions were drastically poorer in the wear resistance than the inventive products. In addition, it is clear from the comparison made between Examples 3 to 5 and Examples 12 to 14 that the effects of preventing wear are even further remarkably exhibited in low-sulfur gas oils having a sulfur content of 0.05% by weight or less.

Table 1

	Compound Example	Sulfur Content in Gas Oil (% by Weight)	Amount * (Parts by Weight)	Scar Diameter (mm)
Example Nos.				
1	Preparation Example 1	0.04	0.005	0.51
2	Preparation Example 2	0.04	0.005	0.49
3	Preparation Example 3	0.04	0.005	0.37
4	Preparation Example 4	0.04	0.005	0.35
5	Preparation Example 5	0.04	0.005	0.29
6	Preparation Example 6	0.04	0.005	0.30
7	Preparation Example 7	0.04	0.005	0.33
8	Preparation Example 8	0.04	0.005	0.52
9	Preparation Example 9	0.04	0.005	0.36
10	Preparation Example 10	0.04	0.005	0.33
11	Preparation Example 11	0.04	0.005	0.57
12	Preparation Example 3	0.20	0.200	0.58
13	Preparation Example 4	0.20	0.200	0.54
14	Preparation Example 5	0.20	0.200	0.50
Comparative Example Nos.				
1	No Additives	0.04	0	0.82
2	No Additives	0.2	0	0.65
3	Comparative Product 1	0.04	0.01	0.61
4	Comparative Product 2	0.04	0.01	0.72

Remark *: Based on 100 parts by weight of the gas oil.

Examples 15 to 28 and Comparative Examples 5 to 8

[0062] In order to evaluate the wear resistance of Compounds 1 to 11 usable in the present invention, Falex test was carried out by a method according to ASTM D 2670-81. V-blocks and pins were immersed in each of the compositions used in Examples 1 to 14. The pin held between the V-blocks was rotated for ten minutes without applying a load, and subsequently, the pin held between the V-blocks was preliminarily rotated for five minutes while applying a load of 100 lbs., and the machine was operated for three hours while applying a load of 150 lbs. The wear amounts of the V-blocks and the pins after operation were measured. The results are shown in Table 2. Incidentally, the test temperature was 25°C at start, and raised to 45° to 50°C by frictional heat during test. The wear amount of each of the gas oil compositions containing Compounds usable in the present invention, namely the gas oil composition of the present invention, is 13.8 mg to 27.5 mg, showing excellent wear resistance. Here, in cases of Examples 15 and 16 using Compounds of Preparation Examples 1 and 2 derived from fatty acids, the performance in preventing wear was slightly reduced as compared with Compounds of Preparation Examples 17 and 18 derived from methyl esters of fatty acids. In the case of Compound of Example 25 where Preparation Example 11 in which diethanolamine remained in an amount of 1% by weight or more was used, although some effects can be observed as compared with Comparative Example 5 where no additives were included, the performance in preventing wear was weak as compared with other Examples. As Comparative Examples, similar tests were carried out with a low-sulfur gas oil (sulfur content: 0.04% by weight) used as a base and with a presently generally commercially available gas oil having a sulfur content of 0.2% by weight. As a result, the wear amounts were 38.0 mg and 32.3 mg, respectively. Also, the wear amount using Comparative Product 1 was 29.3 mg, so that it was found that these comparative gas oil compositions were drastically poorer in the wear resistance than the inventive products. In addition, it is clear from the comparison made between Examples 17 to 19 and Examples 26

to 28 that the effects of preventing wear are even further remarkably exhibited in low-sulfur gas oils having a sulfur content of 0.05% by weight or less.

Table 2

	Compound Example	Sulfur Content in Gas Oil (% by Weight)	Amount * (Parts by Weight)	Wear Amount (mg)
Example Nos.				
15	Preparation Example 1	0.04	0.005	22.1
16	Preparation Example 2	0.04	0.005	20.1
17	Preparation Example 3	0.04	0.005	15.7
18	Preparation Example 4	0.04	0.005	14.5
19	Preparation Example 5	0.04	0.005	13.8
20	Preparation Example 6	0.04	0.005	14.0
21	Preparation Example 7	0.04	0.005	15.7
22	Preparation Example 8	0.04	0.005	22.8
23	Preparation Example 9	0.04	0.005	14.7
24	Preparation Example 10	0.04	0.005	14.5
25	Preparation Example 11	0.04	0.005	25.7
26	Preparation Example 3	0.20	0.200	27.5
27	Preparation Example 4	0.20	0.200	23.1
28	Preparation Example 5	0.20	0.200	20.2
Comparative Example Nos.				
5	No Additives	0.04	0.000	38.0
6	No Additives	0.2	0.000	32.3
7	Comparative Product 1	0.04	0.010	29.3
8	Comparative Product 2	0.04	0.010	35.5

Remark *: Based on 100 parts by weight of the gas oil.

Examples 29 to 42 and Comparative Examples 9 to 12

[0063] In order to evaluate the wear resistance of each of Compounds 1 to 11 usable in the present invention, Soda pendulum-type friction test was carried out. Balls and pins were immersed in each of the gas oil compositions of the present invention used in Examples 1 to 14. The measurement results of the friction coefficients calculated from the attenuation coefficients of the pendulum are shown in Table 3. Lower the friction coefficients, more effective the gas oil compositions become with regard to the lubricity. Incidentally, the test temperature was 25°C. The friction coefficients of the gas oil compositions containing Compounds of the present invention are 0.165 to 0.285, which show that the gas oil compositions have excellent lubricity. Here, in cases of Examples 29 and 30 using Compounds of Preparation Examples 1 and 2 derived from fatty acids, the performance in preventing wear was reduced as compared with Compounds of Examples 31 and 32 derived from methyl esters of fatty acids. In the case of Compound of Example 39 where Preparation Example 11 in which diethanolamine remained in an amount of 1% by weight or more was used, although some effects can be observed as compared with Comparative Example 9 where no additives were included, the performance in preventing wear was weak as compared with other Examples. As Comparative Examples, similar tests were carried out with a low-sulfur gas oil (sulfur content: 0.04% by weight) used as a base and with a presently generally commercially available gas oil having a sulfur content of 0.2% by weight. The friction coefficients were 0.358 and 0.325, respectively. Also, the friction coefficient using Comparative Product 1 was 0.291, so that it was found that these comparative gas oil compositions were drastically poorer in the lubricity than the inventive products. In addition, it is clear from the comparison made between Examples 31 to 33 and Examples 40 to 42 that the effects of preventing wear are even fur-

ther remarkably exhibited in low-sulfur gas oils having a sulfur content of 0.05% by weight or less.

Table 3

	Compound Example	Sulfur Content in Gas Oil (% by Weight)	Amount * (Parts by Weight)	Friction Coefficient
Example Nos.				
29	Preparation Example 1	0.04	0.005	0.241
30	Preparation Example 2	0.04	0.005	0.233
31	Preparation Example 3	0.04	0.005	0.195
32	Preparation Example 4	0.04	0.005	0.175
33	Preparation Example 5	0.04	0.005	0.165
34	Preparation Example 6	0.04	0.005	0.169
35	Preparation Example 7	0.04	0.005	0.168
36	Preparation Example 8	0.04	0.005	0.245
37	Preparation Example 9	0.04	0.005	0.188
38	Preparation Example 10	0.04	0.005	0.171
39	Preparation Example 11	0.04	0.005	0.248
40	Preparation Example 3	0.20	0.005	0.285
41	Preparation Example 4	0.20	0.005	0.279
42	Preparation Example 5	0.20	0.005	0.267
Comparative Example Nos.				
9	No Additives	0.04	0	0.358
10	No Additives	0.2	0	0.325
11	Comparative Product 1	0.04	0.01	0.291
12	Comparative Product 2	0.04	0.01	0.319

Remark *: Based on 100 parts by weight of the gas oil.

[Evaluation Test for Detergency Effect]

Examples 43 to 53 and Comparative Examples 13 to 15

[0064] The detergency performance of the cokes at the injector nozzle portion of diesel engines for each of Compounds 1 to 11 was evaluated by the following method. Specifically, a fuel oil prepared by adding 0.5% by weight of each of Compounds 1 to 11 and Comparative Product 1 to a commercially available gas oil (sulfur content: 0.2% by weight) was loaded on an automobile to carry out test runs with automobiles on city streets. The detergency performance of the cokes at the nozzle portion was evaluated by calculating the ratio of air flow rate in a case where an amount of needle lift was 0.2 mm for an injector nozzle before and after the test runs with automobiles by the following equation:

$$\text{Ratio of Air Flow Rate} = \frac{\text{Air Flow Rate Before or After Detergency Test}}{\text{Air Flow Rate of Brand-New Injector Nozzle}} \times 100$$

[0065] The results of the detergency performance of the injector nozzle tested by the above method are shown in Table 4. Here, "CAROLLA VAN," manufactured by Toyota Motors was used as a tested automobile. When using Preparation Examples 1 to 10, it is clear from Table 4 that the ratio of air flow rate before testing of 19 to 23 were improved as compared to 51 to 81 for after testing, so that high detergency effects of the injector nozzle can be obtained. In the case of using Compound of Preparation Example 11 where 1% by weight or more of diethanolamine remained in the

product, the detergency effects at the injector nozzle was weak. Also, in Comparative Products 1 and 2, such detergency effects could not be observed.

Table 4

	Compound Example	Ratio of Air Flow Rate	
		Before Test	After Test
Example Nos.			
43	Preparation Example 1	22	51
44	Preparation Example 2	19	58
45	Preparation Example 3	23	72
46	Preparation Example 4	21	75
47	Preparation Example 5	20	81
48	Preparation Example 6	22	79
49	Preparation Example 7	21	73
50	Preparation Example 8	23	69
51	Preparation Example 9	23	73
52	Preparation Example 10	22	77
53	Preparation Example 11	21	29
Comparative Example Nos.			
13	No Additives	22	20
14	Comparative Product 1	23	22
15	Comparative Product 2	21	21

[0066] Next, Examples where Compound A and Compound B were used in combination will be explained.

<u>Example Products of Compound B</u>

[0067]

B-1: Polyoxyethylene nonyl phenyl ether (5 mol adduct);
("EMULGEN 905," manufactured by Kao Corporation; HLB = 9.4);
B-2: Monooleate of sorbitan oxyethylene (6 mol) adduct;
("RHEODOL TW-0106," manufactured by Kao Corporation; HLB = 10.0);
B-3: Trioleate of sorbitan oxyethylene (20 mol) and propyleneoxide (5 mol) adduct;
(HLB = 7.6);
B-4: Oleylamine oxyethylene (2 mol) adduct;
("AMITE 402," manufactured by Kao Corporation);
B-5: Oleylamine;
("FARMIN O," manufactured by Kao Corporation);
B-6: Laurylamine;
("FARMIN 20D," manufactured by Kao Corporation);
B-7: Glycerol monooleate;
("EMAZOL MO-50," manufactured by Kao Corporation; HLB = 4.7);

[0068] HLB was calculated in accordance with the description given at page 719 of *Preparation of Surfactants and Their Applications*, 1957, published by Maki Shoten, wherein HLB = 10 × inorganic character/organic character.

Comparative Products of Compound B

[0069]

Comparative Product 3: Monooleate of sorbitol oxyethylene (20 mol) adduct;
("RHEODOL TW-0120," manufactured by Kao Corporation; HLB = 16.3);
Comparative Product 4: Sorbitan trioleate
("RHEODOL SP-030," manufactured by Kao Corporation; HLB = 2.6);

[Evaluation II of Wear Reduction Effects]

Examples 54 to 63 and Comparative Examples 16 to 20

[0070] Each of mixtures of Preparation Examples 5 and 10 of Compound A and Examples 1 to 7 of Compound B (B-1 to B-7) was added in an amount shown in Table 5, to 100 parts by weight of a low-sulfur gas oil having a sulfur content of 0.04% by weight, to prepare a composition. The resulting composition was subjected to a standard test known as a ball-lubricity evaluation test using a cylinder. The test procedures are in accordance with ASTM D 5001-90. In this test, the scar diameter was measured. Here, the smaller the scar diameter, the more effective the additives become regarding wear prevention. In order to make sure that each of these gas oil compositions has excellent storage stability, the gas oil composition was stored at 25°C for one month under a surrounding light condition prior to carrying out the lubricity test. It was confirmed that the formation of precipitates, deterioration by oxidation, discoloration, and the like were not observed in each of the compositions (with the exception for Preparation Example 6 where a slight turbidity was found, so that the composition was heated again to 40°C and then tested). The results obtained are shown in Table 5. The results indicate that each of the gas oil compositions containing Compounds of the present invention having a sulfur content of 0.04% by weight has good wear resistance. The scar diameter of each of the gas oil compositions of Examples 5 and 10, in which Compound A was added alone, was from 0.29 mm and 0.33 mm, respectively, which showed excellent wear resistance in these compositions. It is clear from Examples 54 to 63 that when using Compound A with Compound B, the scar diameter became further small, so that the wear resistance was improved. However, when using Comparative Products 3 and 4, in which HLD was outside the range of 3 to 13, even when Compound A was used in combination with Comparative Product 3 or 4, excellent wear resistance could not be obtained.

Table 5

	Compound A		Compound B		Scar Diameter (mm)
	Compound Example	Amount * (Parts by Weight)	Compound Example	Amount * (Parts by Weight)	
Example Nos.					
5	Preparation Example 5	0.005			0.29
10	Preparation Example 10	0.005			0.33
54	Preparation Example 5	0.0045	B-1	0.0005	0.19
55	Preparation Example 5	0.0045	B-2	0.0005	0.15
56	Preparation Example 5	0.0045	B-3	0.0005	0.19
57	Preparation Example 5	0.0045	B-4	0.0005	0.17
58	Preparation Example 5	0.0045	B-5	0.0005	0.14
59	Preparation Example 5	0.0045	B-6	0.0005	0.20
60	Preparation Example 5	0.0045	B-7	0.0005	0.20
61	Preparation Example 10	0.0045	B-2	0.0005	0.18
62	Preparation Example 10	0.0045	B-4	0.0005	0.19
63	Preparation Example 10	0.0045	B-5	0.0005	0.16
Comparative Example Nos.					
16	No Additives	0			0.82
17	Preparation Example 5	0.0045	Comparative Product 3	0.0005	0.32
18	Preparation Example 5	0.0045	Comparative Product 4	0.0005	0.39
19	Preparation Example 10	0.0045	Comparative Product 3	0.0005	0.45
20	Preparation Example 10	0.0045	Comparative Product 4	0.0005	0.49

Remark *: Based on 100 parts by weight of the gas oil.

Examples 64 to 73 and Comparative Examples 21 to 25

[0071] Each of mixtures of Preparation Examples 5 and 10 of Compound A and Examples 1 to 7 of Compound B (B-1 to B-7) was added in an amount shown in Table 6, to 100 parts by weight of a low-sulfur gas oil having a sulfur content

of 0.04% by weight, to prepare a composition. The resulting composition was subjected to Falex test according to ASTM D 2670-81. V-blocks and pins were immersed in each of the gas oil compositions in which a given amount of the additive was added. The pin held between the V-blocks was rotated for ten minutes without applying a load, and subsequently, the pin held between the V-blocks was preliminarily rotated for five minutes while applying a load of 100 lbs., and the machine was operated for three hours while applying a load of 150 lbs. The wear amounts of the V-blocks and the pins after operation were measured. The results are shown in Table 6. Incidentally, the test temperature was 25°C at start, and raised to 45° to 50°C by frictional heat during test. The wear amount of each of the gas oil compositions containing Compounds usable in the present invention, namely the gas oil composition in which Compound A was added alone (Examples 19 and 24), were 13.8 mg and 14.5 mg, showing excellent performance in preventing wear. However, as shown in Examples 64 to 73, when using Compound A in combination with B, the wear amount became further reduced, so that excellent wear resistance was obtained.

Table 6

	Compound A		Compound B		Wear Amount (mg)
	Compound Example	Amount * (Parts by Weight)	Compound Example	Amount * (Parts by Weight)	
Example Nos.					
19	Preparation Example 5	0.005			13.8
24	Preparation Example 10	0.005			14.5
64	Preparation Example 5	0.0045	B-1	0.0005	11.0
65	Preparation Example 5	0.0045	B-2	0.0005	9.1
66	Preparation Example 5	0.0045	B-3	0.0005	9.9
67	Preparation Example 5	0.0045	B-4	0.0005	9.8
68	Preparation Example 5	0.0045	B-5	0.0005	9.3
69	Preparation Example 5	0.0045	B-6	0.0005	10.2
70	Preparation Example 5	0.0045	B-7	0.0005	10.7
71	Preparation Example 10	0.0045	B-2	0.0005	10.6
72	Preparation Example 10	0.0045	B-4	0.0005	9.9
73	Preparation Example 10	0.0045	B-5	0.0005	9.4
Comparative Example Nos.					
21	No Additives	0			38.0
22	Preparation Example 5	0.0045	Comparative Product 3	0.0005	17.3
23	Preparation Example 5	0.0045	Comparative Product 4	0.0005	18.5
24	Preparation Example 10	0.0045	Comparative Product 3	0.0005	18.9
25	Preparation Example 10	0.0045	Comparative Product 4	0.0005	19.1

Remark *: Based on 100 parts by weight of the gas oil.

Examples 74 to 83 and Comparative Examples 26 to 30

[0072] Each of mixtures of Preparation Examples 5 and 10 of Compound A and Examples 1 to 7 of Compound B (B-1 to B-7) was added in an amount shown in Table 7, to 100 parts by weight of a low-sulfur gas oil having a sulfur content of 0.04% by weight, to prepare a composition. The resulting composition was subjected to Soda pendulum-type friction

test. Balls and pins were immersed in each of the gas oil compositions in which a given amount of the additive was added. The measurement results of the friction coefficients calculated from the attenuation coefficients of the pendulum are shown in Table 7. Lower the friction coefficients, more effective the gas oil compositions become with regard to the lubricity. Incidentally, the test temperature was 25°C. The friction coefficients of the gas oil composition of Examples 33 and 38, in which Compound A of the present invention was added alone, were 0.165 and 0.171, respectively, showing excellent lubricity. However, as shown in Examples 74 to 83, when using Compound A in combination with Compound B, the wear amount became further reduced, so that excellent wear resistance was obtained.

Table 7

	Compound A		Compound B		Friction Coefficient
	Compound Example	Amount * (Parts by Weight)	Compound Example	Amount * (Parts by Weight)	
Example Nos.					
33	Preparation Example 5	0.005			0.165
38	Preparation Example 10	0.005			0.171
74	Preparation Example 5	0.0045	B-1	0.0005	0.137
75	Preparation Example 5	0.0045	B-2	0.0005	0.113
76	Preparation Example 5	0.0045	B-3	0.0005	0.119
77	Preparation Example 5	0.0045	B-4	0.0005	0.121
78	Preparation Example 5	0.0045	B-5	0.0005	0.112
79	Preparation Example 5	0.0045	B-6	0.0005	0.120
80	Preparation Example 5	0.0045	B-7	0.0005	0.127
81	Preparation Example 10	0.0045	B-2	0.0005	0.126
82	Preparation Example 10	0.0045	B-4	0.0005	0.135
83	Preparation Example 10	0.0045	B-5	0.0005	0.127
Comparative Example Nos.					
26	No Additives	0			0.358
27	Preparation Example 5	0.0045	Comparative Product 3	0.0005	0.169
28	Preparation Example 5	0.0045	Comparative Product 4	0.0005	0.181
29	Preparation Example 10	0.0045	Comparative Product 3	0.0005	0.189
30	Preparation Example 10	0.0045	Comparative Product 4	0.0005	0.178

Remark *: Based on 100 parts by weight of the gas oil.

[Test for Storage Stability of Gas Oil]

Examples 84 to 97 and Comparative Examples 31 to 35

[0073] Each of the gas oil composition shown in Table 8 as Examples and Comparative Examples having a sulfur content of 0.04% by weight in which Compound A was added either alone or added in combination with Compound B was allowed to stand under exposure at 60°C to determine the number of days required for precipitating insoluble components in the gas oil compositions. In cases where Compound A was used alone, the number of days required for precipitating insoluble components was about the same as the gas oil containing no additives or the gas oil compositions used in combination with Comparative Example 3 or 4. In cases where Compound A was used in combination with Compound B, the number of days required for precipitating insoluble components was extended, so that excellent storage stability could be obtained.

Table 8

	Compound A		Compound B		Days Until Insoluble Components Are Precipitated
	Compound Example	Amount * (Parts by Weight)	Compound Example	Amount * (Parts by Weight)	
Example Nos.					
84	Preparation Example 5	0.005			4
85	Preparation Example 10	0.005			4
86	Preparation Example 5	0.0045	B-1	0.0005	8
87	Preparation Example 5	0.0045	B-2	0.0005	10
88	Preparation Example 5	0.0045	B-3	0.0005	9
89	Preparation Example 5	0.0045	B-4	0.0005	9
90	Preparation Example 5	0.0045	B-5	0.0005	10
91	Preparation Example 5	0.0045	B-6	0.0005	9
92	Preparation Example 5	0.0045	B-7	0.0005	8
93	Preparation Example 10	0.0045	B-1	0.0005	8
94	Preparation Example 10	0.0045	B-2	0.0005	11
95	Preparation Example 10	0.0045	B-4	0.0005	10
96	Preparation Example 10	0.0045	B-5	0.0005	12
97	Preparation Example 10	0.0045	B-7	0.0005	10
Comparative Example Nos.					
31	No Additives	0			4
32	Preparation Example 5	0.0045	Comparative Product 3	0.0005	4
33	Preparation Example 5	0.0045	Comparative Product 4	0.0005	4
34	Preparation Example 10	0.0045	Comparative Product 3	0.0005	4
35	Preparation Example 10	0.0045	Comparative Product 4	0.0005	4

Remark *: Based on 100 parts by weight of the gas oil.

INDUSTRIAL APPLICABILITY

[0074] By using the gas oil composition of the present invention, there can be exhibited effects in reducing wear of fuel pumps in a system using a gas oil likely to cause wear in fuel pumps, the gas oil having a sulfur content of 0.2% by weight or less, particularly 0.05% by weight or less, and detergency effects of an injection nozzle of diesel engines. Further, an excellent storage ability of the gas oil can be obtained. The effects of the present invention are to satisfy the both the function of preventing wear of the fuel injection pumps during the use of low-sulfur gas oils and the function of detergency effects of stains on the fuel injection nozzle along with the use of the diesel engines, which could not be found in the prior arts.

Claims

1. A gas oil additive for gas oil having a sulfur content of 0.2% by weight or less, characterized in that said gas oil additive contains a compound containing a hydrocarbon group having 10 to 22 carbon atoms, amide group, and hydroxyl group on a carbon atom in β-position to nitrogen atom of said amide group.

2. The gas oil additive according to claim 1, characterized in that the compound as recited in claim 1 is a condensate obtained from one or more monovalent fatty acids having 10 to 22 carbon atoms and one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine.

3. The gas oil additive according to claim 2, characterized in that the monovalent fatty acid as recited in claim 2 is a mixture of fatty acids comprising 70 to 90% by weight of a fatty acid having one unsaturated bond; 5 to 10% by weight of a fatty acid having two unsaturated bonds; and 5 to 20% by weight of a saturated fatty acid.

4. The gas oil additive according to claim 3, characterized in that said mixture of fatty acids contains 68 to 78% by weight of 9-octadecenoic acid.

5. The gas oil additive according to claim 1, characterized in that the compound as recited in claim 1 is a condensate obtained from a fatty acid ester corresponding to the fatty acid as recited in claim 2 or 3 and one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine.

6. The gas oil additive according to claim 5, characterized in that said fatty acid ester contains 68 to 78% by weight of 9-octadecenoic acid ester.

7. The gas oil additive according to any one of claims 2 to 6, characterized in that a total content of one or more compounds selected from monoethanolamine, diethanolamine, mono-2-propanolamine, and di-2-propanolamine which remain therein is 5% by weight or less.

8. The gas oil additive according to claim 1, characterized in that the gas oil additive further contains, in addition to the compound as recited in claim 1, Compound (B) defined below:

   one or more compounds selected from the group consisting of nonionic surfactants having an HLB of 3 to 13; aliphatic amines having 8 to 28 carbon atoms; and alkylene oxide adducts of an aliphatic amine having 8 to 28 carbon atoms, an alkylene oxide moiety having 2 to 3 carbon atoms and a molar addition of 50 mol or less, and that a weight ratio of (A)/(B) is from 1/0.01 to 1/0.5, the compound as recited in claim 1 being defined as Compound (A).

9. The gas oil additive according to claim 8, wherein Compound (A) is a condensate as defined in any one of claims 2 to 7.

10. The gas oil additive according to any one of claims 1 to 9, wherein a sulfur content of the gas oil is 0.05% by weight or less.

11. The gas oil additive according to any one of claims 1 to 10, wherein the gas oil additive is used for the purposes of reducing wear on the contacting surfaces of a metal and deterging a fuel injection nozzle.

12. A gas oil composition having a function of reducing wear and a function of deterging stains, characterized in that the gas oil composition comprises a gas oil having a sulfur content of 0.2% by weight or less and the gas oil additive

according to any one of claims 1 to 11, wherein a content of said gas oil additive is from 0.001 to 1.0 part by weight, based on 100 parts by weight of the gas oil.

13. The gas oil composition according to claim 12, characterized in that a content of the gas oil additive is from 0.001 to 0.1 parts by weight, based on 100 parts by weight of the gas oil.

14. The gas oil composition according to claim 12 or 13, wherein the gas oil has a sulfur content of 0.05% by weight or less.

15. A method of reducing wear in a fuel injection pump comprising using the gas oil composition according to any one of claims 12 to 14.

16. A method of deterging a fuel injection nozzle comprising using the gas oil composition according to any one of claims 12 to 14.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/03312

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl[6] C10L1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl[6] C10L1/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 62-59756, B (Nippon Oil and Fats Co., Ltd.), December 12, 1987 (12. 12. 87) & EP, 117108, A2 & US, 4509954, A & AT, 23357, E & CA, 1218233, A1 & KR, 9000894, B1	1 - 16
A	JP, 6-100517, A (Texaco Development Corp.), April 12, 1994 (12. 04. 94)(Family: none)	1 - 16
A	JP, 6-172286, A (Texaco Development Corp.), June 21, 1994 (21. 06. 94)(Family: none)	1 - 16
A	JP, 6-503836, A (Mobil Oil Corp.), April 28, 1994 (28. 04. 94)(Family: none)	1 - 16
A	JP, 7-17928, A (Texaco Development Corp.), January 20, 1995 (20. 01. 95) & NO, 942348, A & EP, 630959, A1 & US, 5383942, A	1 - 16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
February 4, 1997 (04. 02. 97)	February 12, 1997 (12. 02. 97)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.